UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

DATE: 17-FEB-1999

SUBJECT: PP#8F4925. **Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice.** Amendments of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for Metabolites, Revised Label, Additional Residue, Storage Stability and Rotational Crop Data. MRID#s 445776-01,446897-01 & -02, 446992-01, 446927-01 & -03, 446950-01 & -02, and 447074-01. Chemical 108201. Barcodes D253043, D253041, D244487, D251221 & D251609. Cases 014338 & 289260. Submission#s S539585 & 551777.

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Uniroyal Chemical Company, Inc. has submitted a petition for the establishment of permanent tolerances for residues of the insect growth regulator diflubenzuron and its metabolites in/on the raw agricultural commodities rice grain and rice straw. The proposed tolerances, expressed as diflubenzuron [N-[[(4-chlorophenyl)amino]carbonyl]-2,6-diflourobenzamide] and its metabolites, 4-chlorophenylurea (CPU) and 4-chloroaniline (PCA) are:

Rice, grain	0.02 ppm
Rice, straw	0.8 ppm

The current amendment addresses deficiencies identified in HED's previous review (Memo, G. Kramer 6/23/98; D240107). Data

pertaining to rotational crops (MRID#s 44692701 & 44689703) were reviewed by Dynamac and revised to reflect HED policy.

Executive Summary of Chemistry Deficiencies

- Agency Validation of analytical enforcement methods for residues of PCA and CPU in rice commodities.
- Additional residue data for rice.
- Additional information for limited field rotational crop study.

RECOMMENDATIONS

HED concludes there are no residue chemistry data requirements that would preclude the establishment of the proposed tolerances for diflubenzuron in/on rice. The registration of Dimilin for use on rice should be made conditional upon resolving the deficiencies cited in Conclusions 1, 4b and 5, below. A human-health risk assessment will be prepared as a separate document.

CONCLUSIONS

1. Proposed analytical enforcement methods for PCA and CPU in rice commodities have been submitted. The methods and ILVs have been sent to ACL, Beltsville for PMV (Memo, J. Rowell 12/15/98; D251484). HED will withhold a final conclusion on the adequacy of these method as analytical enforcement methods pending receipt of the PMV reports. However, these methods are based on PAM, Vol. II, Method II (a GC/ECD method that can separately determine residues of diflubenzuron, CPU, and PCA in eggs, milk, and animal tissues). This method has undergone successful Agency validation and is acceptable for enforcement purposes. HED thus has no objections to a conditional registration while the PMV of the methods for PCA and CPU in rice commodities is performed.

2. The results of Multiresidue Method testing of PCA and CPU have been submitted and will be forwarded to FDA.

3. The storage stability of diflubenzuron and CPU in/on rice

commodities have been adequately demonstrated over a 12-month period. PCA is unstable, degrading significantly after 1 month. Therefore, for magnitude of residue samples with storage periods greater than 1 month, correction factors must be used in order to determine the levels of PCA that were present at the time of sample collection.

4a. Residue data from 7 additional trials depicting the magnitude of residue of diflubenzuron and its metabolites in/on rice grain and rice straw were submitted. Two of these trials were conducted at 8X. As all residues in these 2 trials were <LOQ, HED is willing to count these sites towards the total required. The petitioner has also proposed to count the previously reviewed processing trials (MRID 44399306) and the 2 trials for which the samples were reanalyzed. However, residues in excess of the proposed tolerances were observed in these processing studies (performed at a 8X rate) and HED is unwilling to perform a linear extrapolation to 1X in the absence of data to demonstrate this relationship. Also, the length of storage for the samples from the 1995 residue trials (499-542 days) is well outside the range for which storage stability data are available (1 year).

4b. A total of 14 field acceptable trials have been conducted in Regions 4 (9 trials), 6 (2 trials), and 10 (3 trials). As mentioned in the previous memo, HED requires that a minimum of 16 field trials be performed. The Agency suggests the following distribution for the field trials: Regions 4 (11 trials), 5 (1 trial), 6 (2 trial), and 10 (2 trials) (Residue Chemistry Test Guidelines, OPPTS 860.1500 Crop Field Trials Tables 1 and 6). Additional field trials are thus required in Regions 4 (1 trial) and 5 (1 trial). HED recommends against permanent registration of diflubenzuron on rice. However, HED recommends for a conditional registration until the necessary field trials are performed.

4c. No quantifiable residues were found above the respective LOQs (0.01 ppm, 0.01 ppm and 0.005 ppm for diflubenzuron, CPU and PCA, respectively) in any of the samples from the trials submitted with this amendment. The combined residues of diflubenzuron and its metabolites were <0.006 ppm in the treated rice grain and <0.025 ppm in the treated straw samples. In the previously submitted crop field trials, residues of diflubenzuron and PCA in/on treated rice grain were <LOQ for all samples; only two samples bore residues of CPU above the LOQ at 0.002 ppm. The combined residues in/on treated rice grain were <0.017 ppm. Residues of diflubenzuron, CPU and PCA in treated straw samples were <0.01-0.57 ppm, <0.01-0.02 ppm and <0.005-0.021 ppm, respectively, and the combined residues were <0.607 ppm. The available residue data support the proposed tolerances of 0.02 ppm for diflubenzuron in/on rice grain and 0.8 ppm in/on rice straw. A final determination of the appropriate tolerance levels will be withheld pending submission of the additional rice residue data.

5. Uniroyal has submitted data (1998, MRID 44689703) depicting diflubenzuron residues in representative rotational crops from two limited field trials. Provided the petitioner explains the discrepancy in the 0.10 ppm residue value reported for diflubenzuron in one of the wheat forage samples from CA, the limited field rotational crop study is adequate. The available data indicate that tolerances for diflubenzuron residues in rotational crops will not be required provided the Dimilin labels specify a restriction for the planting of rotation crops of at least 30 days. The current label specifies a rotational crop restriction which prohibits the planting of food or feed crops for 6 months following the last application unless it is labeled for use on that crop.

DETAILED CONSIDERATIONS

Deficiency - Conclusion 2 (from Memo, G. Kramer 6/23/98; D240107)

2. The label for the 2 lb/gal FlC should be amended to prohibit the release of flood waters, use of treated waters for the watering of livestock, fishing or farming of crayfish in treated fields and use for drinking or irrigation of crops. **A revised Section B is required.**

Petitioner's Response: The petitioner contends that rice flood waters are not used for the watering of livestock or for drinking water. The proposed label already contains a restriction against use in rice fields where crayfish are farmed. Alternative wording for irrigation is proposed: "Do not use treated rice flood waters for irrigating crops except for uses currently established for Dimilin."

HED's Conclusion: HED concurs that it is unlikely that rice flood waters would be used for the watering of livestock or for drinking water. The restriction on irrigation water is acceptable. This deficiency is now resolved.

Deficiency - Conclusion 5c (from Memo, G. Kramer 6/23/98; D240107)

5c. Analytical enforcement methods are required for residues of PCA and CPU in rice commodities. If the methods used for data collection are proposed for enforcement purposes, then Independent Lab Validations must be submitted prior to initiation of Agency Validation. Specificity of the proposed enforcement methods for residues of PCA and CPU in rice commodities must also be demonstrated.

Petitioner's Response: Submission of:

Dimilin® 2L on Raw and Processed Rice: Processing Study at 8x Rate. Uniroyal Study Sponsor Study No. RP-96013. Appendix C of Appendix VII of MRID# 44399306 (pages 291-512).

Independent Laboratory Validation of the Method for the Analysis of 4-Chlorophenyl Urea (CPU) in Rice Commodities as 'Described in: Dimilin 25W on Raw and Processed Rice: Processing Study at 8x Rate,' in Compliance with OPPTS 860.1340. Document Number: 7691-98-0173-CR-001. Sponsor ID: RP-98030. Study Completed: 10/22/98. Ricerca, Inc. MRID# 44695001.

Method Validation for 4-Chloroaniline (PCA) at Low Levels Using Isotope Dilution in Rice and Rice Commodities. PTRL Report No. 645W-1. MRID# 44399303.

Independent Laboratory Validation of: Determination of 4-Chloroaniline (PCA) at Low Levels Using ^{13}C-PCA as an Internal Standard in Rice Commodities in Compliance with OPPTS 860.1340. Document Number: 7621-98-0119-CR-001. Sponsor: ID RP-98027. Study Completed: 9/25/98. Ricerca, Inc. MRID# 44695002.

Specificity of the Analytical Method for 4-Chlorophenyl Urea and Parachloroaniline. Project No. 98219. MRID# 44689701.

Specificity (MRID# 44689701): Specificity testing for PCA is not required as this method uses GC-MSD. The specificity of CPU was investigated by performing an interference study with 19 different pesticides. None were found to interfere with CPU. These compounds included all the halogenated pesticides for which tolerances are established on rice.

HED's Conclusion: The requested information has been provided. The methods and ILVs have been sent to ACL, Beltsville for PMV (Memo, J. Rowell 12/15/98; D251484). HED will withhold a final conclusion on the adequacy of these method as analytical enforcement methods pending receipt of the PMV reports. However, these methods are based on PAM, Vol. II, Method II (a GC/ECD method that can separately determine residues of diflubenzuron, CPU, and PCA in eggs, milk, and animal tissues). This method has undergone successful Agency validation and is acceptable for enforcement purposes. HED thus has no objections to a conditional registration while the PMV of the methods for PCA and CPU in rice commodities is performed.

Deficiency - Conclusion 5d (from Memo, G. Kramer 6/23/98; D240107)

5d. The FDA PESTDATA database dated 1/94 (PAM Vol. I, Appendix II) contains no information on DFB recovery using Multiresidue methods PAM, Vol. I Sections 302, 303 and 304. However, the petitioner has submitted Multiresidue testing data on DFB *per se* (MRID 42895401) that the Agency has forwarded to the FDA. Multiresidue testing data on CPU and PCA remain outstanding.

Petitioner's Response: Submission of:

> Multiresidue Method Testing for p-Chloroaniline and 4-Chlorophenyl Urea in Rice Grain and Soybeans. Sponsor ID: RP-98028. MRID# 44707401.

For Protocol D validation of PCA using rice, recoveries ranged from 23-43% at fortifications of 0.10 and 0.55 ppm. CPU was not recovered through any Protocol.

HED's Conclusion: The results of Multiresidue Method testing of PCA and CPU have been submitted and will be forwarded to FDA. The requested information has been provided. This deficiency is now resolved.

Deficiency - Conclusion 6 (from Memo, G. Kramer 06/23/98)

6. No storage stability data were submitted with this petition, and no applicable storage stability data were available in the RED that was issued in 3/95. The petitioner has indicated that a storage stability study supporting the sample storage data associated with this petition is in progress. RAC samples were stored frozen (<0°C) and analyzed for DFB residues within 30-76 days of harvest and within 174-228 days for CPU and PCA residues. Processed commodities were stored at -18°C for 72-139 days prior to extraction and analysis. Samples of treated rice flood waters were stored frozen and analyzed for residues of DFB within 214-250 days of collection.

Petitioner's Response: Submission of:

> Storage Stability of Diflubenzuron and its Metabolites (PCA and CPU) in Rice and Rice Commodities. MRID# 44689702.

Data from a 12-month storage stability study were submitted depicting the magnitude of residue of diflubenzuron and its metabolites 4-chlorophenylurea (CPU) and parachloroaniline (PCA) in/on rice grain, straw, bran and hulls (MRID# 44699202). Frozen untreated rice samples (grain, barley, straw, and hulls) were provided by Uniroyal Chemical Company, Inc. The samples were fortified with a 0.1 ppm diflubenzuron, CPU, and PCA. The samples were stored frozen (temperature range of -12 to -25°C) until analysis at approximately 0, 1, 3, 6, 9 and 12 months after fortification. At each analysis date (except duplicate analysis at time zero), three freshly fortified control samples and two aged

samples were analyzed in order compare the percent recovery of diflubenzuron, PCA, and CPU from aged vs. freshly fortified samples. Three methods appropriate for each analyte were used to determined the recoveries. Tables 1-3 summarize the storage stability for the control rice commodities spiked with diflubenzuron, CPU and PCA respectively.

Table 1: Summary of Storage Stability for Control Rice Products Spiked with Diflubenzuron.

Commodity	Residue Level (ppm)	Storage Period (Months)	Average Fresh Fortification Recovery (%)	Average Apparent Recovery in Stored Sample (%)	Average Corrected Recovery in Stored Sample (%)
Rice Grain	0.1	0	79	NA	NA
	0.1	30	95	93	98
	0.1	91	80	57	71
	0.1	224	52	43	82
	0.1	287	90	51	56
	0.1	345	71	59	82
Rice Bran	0.1	0	101	NA	NA
	0.1	28	106	106	100
	0.1	89	78	59	74
	0.1	228	11	11	96
	0.1	313	68	78	114
	0.1	365	52	55	106
Rice Straw	0.1	0	103	NA	NA
	0.1	41	89	93	104
	0.1	90	85	53	63
	0.1	222	80	45	55
	0.1	285	88	76	86
	0.1	355	45	57	125
Rice Hulls	0.1	0	103	NA	NA
	0.1	34	98	116	118
	0.1	92	88	59	67
	0.1	230	77	52	68
	0.1	295	70	40	57
	0.1	350	63	61	96

Table 2: Summary of Storage Stability for Control Rice Products Spiked with CPU.

Commodity	Residue Level (ppm)	Storage Period (Months)	Average Fresh Fortification Recovery (%)	Average Apparent Recovery in Stored Sample (%)	Average Corrected Recovery in Stored Sample (%)
Rice Grain	0.1	0	85	NA	NA
	0.1	28	81	74	90
	0.1	123	78	47	61
	0.1	183	71	44	61
	0.1	283	72	70	97
	0.1	343	78	55	71
Rice Bran	0.1	0	101	NA	NA
	0.1	29	90	102	113
	0.1	123	86	38	44
	0.1	186	98	73	74
	0.1	290	106	81	76
	0.1	338	99	103	103
Rice Straw	0.1	0	108	NA	NA
	0.1	29	87	99	114
	0.1	92	87	89	102
	0.1	186	124	99	80
	0.1	295	109	127	116
	0.1	343	117	100	85
Rice Hulls	0.1	0	72	NA	NA
	0.1	42	74	81	109
	0.1	88	85	44	51
	0.1	190	74	33	44
	0.1	290	91	47	51
	0.1	346	57	42	73

Table 3: Summary of Storage Stability for Control Rice Products Spiked with PCA.

Commodity	Residue Level (ppm)	Storage Period (Months)	Average Fresh Fortification Recovery (%)	Average Apparent Recovery in Stored Sample (%) [a]
Rice Grain	0.1	0	91	NA
	0.1	27	98	40
	0.1	87	103	27
	0.1	175	94	29
	0.1	273	89	23
	0.1	336	87	23
Rice Bran	0.1	0	96	NA
	0.1	27	102	52
	0.1	87	104	36
	0.1	175	98	34
	0.1	273	87	35
	0.1	336	86	31
Rice Straw	0.1	0	101	NA
	0.1	27	100	67
	0.1	90	97	49
	0.1	175	85	40
	0.1	273	104	42
	0.1	336	89	37
Rice Hulls	0.1	0	100	NA
	0.1	27	100	65
	0.1	90	97	48
	0.1	175	77	30
	0.1	273	88	42
	0.1	336	91	30

a. The aged samples were not corrected for concurrent fortification due to the use of an internal standard.

HED's Conclusion: Diflubenzuron was determined to be stable over a 12-month period with average recoveries of 78% (grain), 99% (bran), 89% (straw), and 78% (hulls). CPU exhibited the following average recoveries of a 12 month period: 76% (grain), 99% (bran),

89% (straw), and 78% (hulls). Significant declines in the PCA concentration were observed, decreasing rapidly to 56% (average) after 1 month and to 30% (average) after 12 months.

The total frozen storage intervals between harvest and sample analysis of the rice grain samples were 9-49 days (diflubenzuron analysis), 9-48 days (CPU analysis) and 22-44 days (CPA analysis). The total frozen storage intervals for the rice straw samples were 21-51 days (diflubenzuron analysis), 41-58 days (CPU analysis) and 16-56 days (CPA analysis). In the previously submitted crop field trials (1997, MRID# 44399305), RAC samples were held frozen at <0°C for 14-24 days and 119-208 days between sampling and analyses for residues of diflubenzuron and CPU/PCA, respectively. The total storage time from harvest to analysis was 30-76 days (diflubenzuron analysis) and 174-228 days (CPU and PCA analysis).

The storage stability of diflubenzuron and CPU in/on rice commodities have been adequately demonstrated over a 12-month period. PCA is unstable, degrading significantly after 1 month. Therefore, for magnitude of residue samples with storage periods greater than 1 month, correction factors must be used in order to determine the residue levels that were present at the time of sample collection.

Deficiency - Conclusions 9a, 9b, & 9c (Memo, G. Kramer 06/23/98)

9a. A total of 7 field trials were conducted with rice in Regions 4 (5 trials), 6 (1 trial), and 10 (1 trial). In addition, trials were conducted in CA (1) and MS (1) to support a temporary tolerance petition for an EUP (1995, MRID 44080001). Residue data arising from the petitioner's petition for an EUP are not adequate to support a tolerance expression based on "the combined residues of diflubenzuron and metabolites convertible to p-chloroaniline, expressed as based on diflubenzuron" as defined by the HED Metabolism Committee (3/22/94). The study did not address CPU residue levels or PCA residues in straw, and the method recovery of PCA in grain (~50%) is below the acceptable range at the LOQ (0.025 ppm).

9b. The number and location of field trials are inadequate to support the proposed use of the 2 lb/gal FlC on rice. HED notes that this study was initiated in 1996, well after the issuance of residue chemistry test guidelines delineating field trial distribution by region/crop ("EPA Guidance on Number and Location of Domestic Crop Field Trials for Establishment of Pesticide Residue Tolerances," E. Saito and E. Zager, 6/2/94). A total of 16 field trials are required for rice in Regions 4 (11 trials), 5 (1 trial), 6 (2 trials), and 10 (2 trials). HED recommends that the petitioner conduct an additional 9 rice trials in Regions 4 (6 trials), 5 (1 trial), 6 (1 trial), and 10 (1 trial).

9c. A determination of the appropriate tolerance levels will be withheld pending submission of storage stability data and the additional rice residue data.

Petitioner's Response: Submission of:

Dimilin® 2L on Rice: Magnitude of Residue Study. MRID# 44699201.

Dimilin® 25W in Raw and Processed Rice: Processing Study at 8X Rate. MRID# 44577601.

Residue data were submitted depicting the magnitude of residue of diflubenzuron and its metabolites 4-chlorophenylurea (CPU) and parachloroaniline (PCA) in/on rice grain and rice straw (MRID# 44699201). Five field trials were conducted in the following states: CA(1), LA(3), and TX(1). Dimilin® 2L was applied at a rate of 1.0 lbs./A (0.25 lbs. a.i./A, 1X). The applications consisted of either 1 x 1.0 lbs./A or 2 x 0.5 lbs./A. A spray volume of 10-15 gallons/A was applied to seeded rice in the 3- to 4-leaf stage under post permanent flood conditions. Applications were made using aerial equipment in the California and Texas sites. Applications were made via ground application equipment in two of Louisiana sites, and by aerial equipment in the third. At each trial site, two rice grain and straw samples were taken from the treated plot, and one of each was taken from the untreated plot. The PHIs were 83-101 days. Following collection, the samples were placed in frozen storage. The samples were shipped frozen via overnight carrier to be analyzed for diflubenzuron, CPU and PCA. The limits of quantitation were 0.01 ppm, 0.01 ppm and 0.005 ppm for diflubenzuron, CPU and PCA, respectively. No residues were found above the respective LOQs in any of the treated and untreated samples. A summary of the residues of diflubenzuron and its metabolites in rice grain and rice straw are listed in Tables 4 and 5, respectively.

Table 4. Residues of Diflubenzuron and its Metabolites in Rice Grain.

Trial Location	Uniroyal Sample ID	Typea	DFB (ppm)	CPU (ppm)	PCA (ppm)
Louisiana KAG-98010	K-98-518	C	ND	ND	<0.005
	K-98-519	T	ND	ND	<0.005
	K-98-520	T	ND	<0.001	<0.005
Louisiana KAG-98011	K-98-524	C	ND	ND	<0.005
	K-98-525	T	ND	ND	<0.005
	K-98-526	T	ND	<0.001	<0.005
Louisiana KAG-98012	K-98-530	C	ND	ND	<0.005
	K-98-531	T	ND	ND	<0.005
	K-98-532	T	ND	ND	<0.005
California KAG-98015	K-98-500	C	ND	ND	<0.005
	K-98-501	T	ND	<0.001	<0.005
	K-98-502	T	ND	<0.001	<0.005
Texas KAG-98013	K-98-506	C	ND	ND	<0.005
	K-98-507	T	ND	ND	<0.005
	K-98-508	T	ND	ND	<0.005

a C = Control; T = Treated
NR = Not Reported; ND = Not Detected

Table 5. Residues of Diflubenzuron and its Metabolites in Rice Straw.

Trial Location	Uniroyal Sample ID	Type	DFB (ppm)	CPU (ppm)	PCA (ppm)
Louisiana KAG-98010	101	C	<0.01	<0.01	<0.005
	301	C	ND	<0.01	<0.005
	406	C	ND	<0.01	<0.005
	107	T	ND	<0.01	<0.005
	203	T	ND	ND	<0.005
	404	T	ND	ND	<0.005
Louisiana KAG-98011	K-98-527	C	ND	ND	<0.005
	K-98-528	T	ND	ND	<0.005
	K-98-529	T	ND	ND	<0.005

Trial Location	Uniroyal Sample ID	Type	DFB (ppm)	CPU (ppm)	PCA (ppm)
Louisiana KAG-98012	K-98-533	C	ND	<0.01	<0.005
	K-98-534	T	ND	<0.01	<0.005
	K-98-535	T	ND	<0.01	<0.005
California KAG-98015	K-98-503	C	ND	ND	<0.005
	K-98-504	T	<0.01	<0.01	<0.005
	K-98-505	T	<0.01	ND	<0.005
Texas KAG-98013	K-98-509	C	ND	0.01	ND
	K-98-510	T	<0.01	ND	<0.005
	K-98-511	T	<0.01	ND	<0.005

a C = Control; T = Treated
NR = Not Reported; ND = Not Detected

Laboratory fortified samples were analyzed concurrently with the field samples. The average recoveries of diflubenzuron were 82 ± 24% for grain and 82 ± 17% for straw. The average recoveries of CPU were 101 ± 26% for grain and 85 ± 37% for straw. The average recoveries for PCA were 89 ± 5% for grain and 85 ± 4% for straw.

Uniroyal Chemical Company submitted the following data (1998, MRID 44577601) depicting the potential for concentration of diflubenzuron residues in the processed commodities of rice. Two trials were conducted in MS(1) and CA(1). At each site, rice grain and straw were harvested at maturity, 3-4 months following a post-permanent flood application of the 25W formulation at 2 lb ai/A (8x the proposed maximum application rate). One control and two treated samples each of rice grain and straw were collected. Samples were processed according to simulated commercial procedures into hulls, bran and polished rice. Samples were placed in frozen storage (<0°C) and were homogenized with dry ice (except bran) prior to analysis; the total interval from harvest of samples to analysis was 351-387 days. Residues in/on treated and untreated rice commodities were determined using GC/ECD and GC/MS as described previously. Residues of diflubenzuron, PCA, and CPU were <LOQ (0.01 ppm for diflubenzuron and CPU and 0.005 for PCA in straw; 0.01 ppm for diflubenzuron, 0.001 ppm for CPU and 0.005 for PCA in grain) in all treated samples of the RAC and processed commodities of rice.

Additionally, rice grain and straw samples from the 2 locations (MS and CA) of the 1995 residue study were reanalyzed using GC/ECD and GC/MS as described previously. The study was not acceptable for the permanent tolerance petition as it did not address CPU residue

levels or PCA residues in straw, and the method recovery of PCA in grain (~50%) was below the acceptable range at the LOQ (0.025 ppm). Upon reanalysis, residues of diflubenzuron PCA and CPU were <LOQ (0.01 ppm for diflubenzuron and CPU and 0.005 for PCA) in all samples. The total interval from harvest of samples to analysis was 499-542 days.

HED's Conclusions: Residue data from 7 additional trials depicting the magnitude of residue of diflubenzuron and its metabolites in/on rice grain and rice straw were submitted. Two of these trials were conducted at 8X. As all residues in these 2 trials were <LOQ, HED is willing to count these sites towards the total required. The petitioner has also proposed to count the previously reviewed processing trials (MRID 44399306) and the 2 trials for which the samples were reanalyzed. However, residues in excess of the proposed tolerances were observed in these processing studies (performed at a 8X rate) and HED is unwilling to perform a linear extrapolation to 1X in the absence of data to demonstrate this relationship. Also, the length of storage for the samples from the 1995 residue trials (499-542 days) is well outside the range for which storage stability data are available (1 year). Therefore, a total of 14 field acceptable trials have been conducted in Regions 4 (9 trials), 6 (2 trials), and 10 (3 trials). As mentioned in the previous memo, HED requires that a minimum of 16 field trials be performed. The Agency suggests the following distribution for the field trials: Regions 4 (11 trials), 5 (1 trial), 6 (2 trial), and 10 (2 trials) (Residue Chemistry Test Guidelines, OPPTS 860.1500 Crop Field Trials Tables 1 and 6). Additional field trials are thus required in Regions 4 (1 trial) and 5 (1 trial). The petitioner has questioned the need for a residue trial in Region 5. However, a trial in this Region is required as MO is fifth largest producer of long-grain rice in the US (Ag. Stats. 1995-96). **This deficiency remains outstanding; therefore, HED recommends against permanent registration of diflubenzuron on rice.** However, HED recommends for a conditional registration until the necessary field trials are performed.

No quantifiable residues were found above the respective LOQs (0.01 ppm for diflubenzuron and CPU and 0.005 for PCA in straw; 0.01 ppm for diflubenzuron, 0.001 ppm for CPU and 0.005 for PCA in grain) in any of the samples from the trials submitted with this amendment. The combined residues of diflubenzuron and its metabolites were <0.005-<0.006 ppm in the treated rice grain and <0.005-<0.025 ppm in the treated straw samples. In the previously submitted crop field trials, residues of diflubenzuron and PCA in/on treated rice grain were <LOQ for all samples; only two samples bore residues of CPU above the LOQ at 0.002 ppm. The combined residues in/on treated rice grain were <0.016-<0.017 ppm. Residues of diflubenzuron, CPU and PCA in treated straw samples were <0.01-0.57 ppm, <0.01-0.02 ppm and <0.005-0.021 ppm, respectively, and the combined residues were <0.025-<0.607 ppm.

Previously, the HED Metabolism Committee concluded (S. Knizner, 3/22/94) that tolerances should be expressed in terms of the combined residues of diflubenzuron and metabolites convertible to PCA (CPU and PCA) expressed as diflubenzuron. The available residue data support the proposed tolerances of 0.02 ppm for diflubenzuron in/on rice grain and 0.8 ppm in/on rice straw. A final determination of the appropriate tolerance levels will be withheld pending submission of the additional rice residue data.

Deficiency - Conclusion 10 (from Memo, G. Kramer 6/23/98; D240107)

10. The submitted rice processing study is adequate, provided that supporting storage stability data are submitted. Residues of diflubenzuron did not concentrate in rice fractions processed from grain treated at 8x and bearing residues of 0.27 and 0.87 ppm. PCA and CPU concentrated ~1.1-4.1x in hull and bran fractions from nondetectable levels in the RAC. However, these components represent a very small proportion of the total residue and overall combined residues did not concentrate. Tolerances for residues in rice processed commodities are not required.

Petitioner's Response: Submission of:

> Storage Stability of Diflubenzuron and its Metabolites (PCA and CPU) in Rice and Rice Commodities. MRID# 44689702.

HED's Conclusion: The storage stability of diflubenzuron and CPU in/on rice commodities have been adequately demonstrated. This deficiency is now resolved.

Deficiency - Conclusion 11 (from Memo, G. Kramer 6/23/98; D240107)

11a. If the petitioner amends the Dimilin® 2L label to specify a 12-month plantback interval (PBI) for rotational crops, then no limited rotational residue data are required on leafy vegetables, root and tuber vegetables, and grain forages. However, limited rotational field studies using a representative cereal grain at two sites are required to determine the need for tolerances on rotation cereal crops (data are required for straw, grain and hulls, not forage).

11b. If the petitioner prefers to maintain the 6-month PBI currently specified on the Dimilin® 2L label, then limited rotational field studies are required at two sites using a representative leafy vegetable, root and tuber vegetable, and a cereal grain. The six trials should be conducted on a specific crop in each of the three crop groups which the petitioner intends to have as a rotational crop on the label.

11c. Alternatively, the petitioner may amend the Dimilin® 2L label to specify a 12-month PBI for rotational leafy vegetables, root and tuber vegetables, and forage crops; and to prohibit rotation to all other crops (except registered crops).

Petitioner's Response: Submission of:

> 44692701. Hathcock, T.; Ruzo, L. (1998) Storage Stability of Diflubenzuron and Its Metabolites (PCA and CPU) in

Rotational Crop Commodities: Lab Project Crop Commodities: Lab Project Number: RP-97027: 692W-1: 692W. Unpublished study prepared by PTRL West, Inc. 574 p.

44689703. Gaydosh, K. (1998) Dimilin 25W Rotational Crop Study: Dimilin 25W Treated Cotton Rotated with Wheat, Lettuce, and Turnips 30, 45, 60, 90, 120, 180 and 365 Days After Harvest: Lab Project Number: RP-95018: CEJ-95002: AWD-95904. Unpublished study prepared by PTRL West, Inc. and ABC Laboratories. 1195 p.

Residue Analytical Methods

In conjunction with the rotational crop field trials (MRID 44689703), Uniroyal submitted descriptions of three separate analytical methods for the respective determination of diflubenzuron, CPU, and PCA in plant commodities, along with method validation data. The method for diflubenzuron involves isolation and hydrolysis of diflubenzuron to PCA, which is subsequently derivatized with heptafluorobutyric anhydride (HFBA) and analyzed by GC/ECD. This method is similar to the current enforcement method (PAM Vol. II, Method I). The method for CPU is also a GC/ECD method in which CPU is isolated and derivatized with HFBA prior to analysis. The method for PCA is a GC/MS method which quantifies the HFBA derivative of PCA and uses ^{13}C-PCA as an internal standard.

All three of these methods were recently reviewed in conjunction with a petition for the use of diflubenzuron on rice (PP#8F4925, DP Barcode D240107, G. Kramer, 6/23/98) and were deemed adequate for data collection. The GC/ECD method for CPU and the GC/MS method for PCA have also undergone successful independent laboratory validations and have been forwarded to the Analytical Chemistry Branch for an Agency validation (DP Barcode D251484, J. Rowell, 12/15/98). A brief description of each of these methods is provided below.

GC/ECD Method for diflubenzuron. Residues are extracted from plant samples with dichloromethane (DCM), filtered, concentrated, and redissolved in DCM:petroleum ether (3:25, v/v). Residues are then cleaned up using a Florisil column eluted sequentially with acetone:petroleum ether at 1:9 and 1:4 (v/v), and concentrated to dryness. The isolated diflubenzuron is then hydrolyzed in 85% H_3PO_4 (reflux 30 minutes) to PCA which is partitioned into hexane under acidic and basic conditions. The PCA residues are then derivatized with HFBA prior to GC/ECD analysis. The validated limit of quantitation (LOQ) for diflubenzuron in/on lettuce, turnip, and wheat commodities is 0.01 ppm.

GC/ECD Method for CPU. Residues of CPU are extracted with ethyl

acetate, filtered, concentrated and redissolved in acetone:petroleum ether (1:5, v/v). Residues are then cleaned up using a silica gel column eluted sequentially with acetone:petroleum ether (20:80, v/v), ethanol:petroleum ether (15:85, v/v), and ethanol:petroleum ether (30:70, v/v). Residues in the final eluant are concentrated to dryness, redissolved in acetonitrile, and derivatized with HFBA. The derivatized CPU is diluted with H_2O:saturated sodium carbonate (4:0.5, v/v), partitioned into hexane and analyzed by GC/ECD. The validated LOQ for CPU is 0.01 ppm in/on lettuce, turnip roots and tops, and wheat forage, grain, and straw and 0.05 ppm in/on wheat hay.

GC/MS Method for PCA. For analysis of PCA, plant samples are fortified with ^{13}C-PCA as an internal standard prior to analysis. The residues of PCA and the internal standard are hydrolyzed in 0.1N HCl (60°C for 30 minutes), cooled and filtered. Residue are then adjusted to pH>12 with 50% NaOH, salinized with NaCl, and partitioned into hexane. The residues are partitioned into 0.1 N HCl, readjusted to pH >12 with 50% NaOH, partitioned back into hexane. The organosoluble residues are then cleaned up using a Florisil column eluted with 20% acetone in hexane. Residues are derivatized with HFBA and analyzed by GC/MS in the SIM mode using ions 323, 329, 126 and 132. The validated LOQ for PCA is 5 ppb in/on lettuce, turnip, and wheat commodities.

For validation of the GC/ECD methods, the analytical laboratory (PTRL West, Inc., Richmond, CA) separately fortified duplicate control samples of each plant matrix at 0.01, 0.05, and 0.10 ppm with diflubenzuron and CPU, and analyzed these fortified samples along with duplicate control samples. For validation of the GC/MS method, control samples of each matrix (except wheat hay) were fortified at 1, 5, and 10 ppb with PCA and analyzed along with duplicate control samples. Apparent residues of diflubenzuron and CPU were <LOQ (<0.01 ppm) in duplicate controls of each commodity except wheat hay, which had apparent residues of CPU at 0.012 ppm. Apparent residues of PCA were also <LOQ (<0.001 ppm) in duplicate controls of each commodity except wheat grain and straw. Apparent PCA residues were 0.9 and 1.1 ppb in grain and 0.9 and 1.2 ppb in straw. Results of these method validations are presented in Table 6.

With a few exceptions, overall recoveries of each analyte were acceptable (70-120%). In wheat straw, recoveries of diflubenzuron at 0.01 ppm and CPU at 0.1 ppm were somewhat low (64-69%), and recoveries of CPU from wheat hay were high (~128%) at of the lowest fortification (0.01 ppm) due to matrix interference. For all matrices, average recoveries were 81-104% for diflubenzuron, 73-106% for CPU, and 90-109% for PCA. Although recoveries of PCA were acceptable at the 1 ppb fortifications, the analytical laboratory determined that the LOQ for the GC/MS method should be 5 ppb because of apparent residues of PCA at or just below the 1 ppb

level in a number of control samples.

In addition to the method validation trial, the analytical laboratory provided method recovery data from fortified samples analyzed concurrently with the rotational crop field trial samples. For these analyses, one control and four treated field samples of each commodity were generally analyzed for each analyte at each plant-back interval (PBI) and test site. Each sample set also included two control samples fortified with either diflubenzuron or CPU at 0.03 ppm or PCA at 5 ppb. A total of 18-26 fortified samples were analyzed for each analyte in each commodity. Overall recoveries of diflubenzuron were 70-121% for all commodities and averaged 85-102% (Table 7). For CPU, overall recoveries were 56-120% and averaged 85-102%. For PCA, overall recoveries were 71-132% and averaged 91-102%.

The GC/ECD methods for diflubenzuron and CPU and the GC/MS method for PCA are adequate for data collection. In lettuce, turnip, and wheat commodities, the LOQs for diflubenzuron and PCA are 0.01 ppm and 5 ppb, respectively. For CPU, the LOQ is 0.01 ppm in lettuce and wheat commodities, but is 0.03 ppm in turnip roots and tops. The higher LOQ for CPU in turnips is due to matrix interferences that were apparent in control samples.

Table 6. Method validation data for the GC/ECD methods for determining diflubenzuron and CPU, and the GC/MS method for determining PCA in various rotational crop commodities.

Analyte	Matrix	Fortification levels (ppm)	Number of samples	Range of Recoveries	Average Recovery ± S.D.
DFB	Lettuce	0.01-0.10	6	91-132 (1) [a]	104 ± 17
	Turnip tops	0.01-0.10	6	74-90	83 ± 7
	Turnip roots	0.01-0.10	6	80-103	88 ± 11
	Wheat forage	0.01-0.10	6	92-119	104 ± 11
	Wheat hay	0.01-0.10	6	87-115	101 ± 11
	Wheat grain	0.01-0.10	6	84-110	101 ± 13
	Wheat straw	0.01-0.10	6	64-98 (2)	81± 10
CPU	Lettuce	0.01-0.10	6	95-112	105 ± 7
	Turnip tops	0.01-0.10	6	89-110	99 ± 9
	Turnip roots	0.01-0.10	6	103-110	106 ± 3
	Wheat forage	0.01-0.10	6	81-106	91 ± 11
	Wheat hay	0.01-0.10	6	83-128 (2) [b]	102 ± 21
	Wheat grain	0.01-0.10	6	80-94	86 ± 6
	Wheat straw	0.01-0.10	6	69-77 (2)	73 ± 4
PCA	Lettuce	0.001-0.01	6	88-105	100 ± 6
	Turnip tops	0.001-0.01	6	90-103	98 ± 4
	Turnip roots	0.001-0.01	6	80-102	97 ± 8
	Wheat forage	0.001-0.01	6	106-115	109 ± 3
	Wheat grain [c]	0.001-0.01	6	81-99	90 ± 7
	Wheat straw [c]	0.001-0.01	6	74-106	92 ± 12

[a] Values listed in parentheses represent the number of samples with a recovery outside the acceptable 70-120% range.

[b] Recoveries of CPU from wheat hay at 0.01 ppm were 127 and 128%; apparent residues of CPU in control samples were 0.012 ppm.

[c] Apparent residues of PCA were 0.9 and 1.1 ppb in the two grain controls, and 0.9 and 1.2 ppb in the two straw controls.

Table 7. Concurrent method recoveries from control samples fortified with diflubenzuron (DFB) or CPU at 0.03 ppm or PCA at 5 ppb and analyzed in conjunction with the field rotational crop samples.

Analyte	Matrix	Fortification levels (ppm)	Number of samples	Range of Recoveries	Average Recovery ± S.D.
DFB	Lettuce	0.03	26	70-101	85 ± 8
	Turnip tops	0.03 [a]	24	72-119	98 ± 16
	Turnip roots	0.03	24	70-119	99 ± 13
	Wheat forage	0.03	18	72-118	100 ± 14
	Wheat hay	0.03	22	74-106	85 ± 9
	Wheat grain	0.03	20	73-116	94 ± 15
	Wheat straw	0.03	22	79-121 (1) [b]	102 ± 12
CPU	Lettuce	0.03	26	71-115	85 ± 12
	Turnip tops	0.03	24	69-118 (1)	98 ± 14
	Turnip roots	0.03	24	56-120 (1)	102 ± 16
	Wheat forage	0.03	18	75-117	95 ± 12
	Wheat hay	0.03	22	61-117 (4)	90 ± 16
	Wheat grain	0.03	20	68-115 (2)	87 ± 14
	Wheat straw	0.03	22	78-120	99 ± 13
PCA	Lettuce	0.005	26	76-111	98 ± 6
	Turnip tops	0.005	24	71-102	94 ± 7
	Turnip roots	0.005	24	88-108	99 ± 7
	Wheat forage	0.005	18	87-115	101 ± 7
	Wheat hay	0.005	21	83-111	98 ± 7
	Wheat grain	0.005	20	79-104	91 ± 8
	Wheat straw	0.005	22	76-132 (1)	102 ± 11

[a] One turnip top sample was fortified with diflubenzuron at 0.06 ppm.
[b] Values listed in parentheses represent the number of samples with a recovery outside the acceptable 70-120% range.

Storage Stability Data

To support the field rotational crop study, Uniroyal submitted data (1998, MRID 44692701) depicting the stability of diflubenzuron, CPU and PCA in representative frozen rotational crop matrices. Control samples of lettuce, turnip roots, and wheat hay and grain were separately fortified with either diflubenzuron, CPU, or PCA each at 0.1 ppm and stored at <0 °C and analyzed after approximately 0, 1, 3, 6, 9, and 12 months of storage. Samples were analyzed using the adequate GC/ECD and GC/MS methods described above. For each matrix and analyte, at least two stored fortified samples were analyzed along with two freshly fortified samples and a control sample at each interval, except for the 0-time point.

Although there was some variability in the recovery of residues over time, the submitted storage stability data are adequate and

indicate that residues of diflubenzuron *per se* are stable for up to 12 months in lettuce, turnip roots, and wheat grain. After ~13 months of storage, there was a slight decline (27%) in residues of diflubenzuron in wheat hay (Table 8). Residues of CPU were stable for up to 12 months in turnip roots and wheat hay, and declined slightly (22%) in lettuce by 12 months (Table 9). In wheat grain, CPU declined by ~50% after 12 months of storage. Residues of PCA were not stable in any of the matrices tested. After one month of storage, PCA declined by 57% in lettuce, 22% in turnip roots, 32% in wheat grain, and 31% in wheat hay (Table 10). After an initial rapid decline, residues of PCA declined more slowly. After 12 months of storage, PCA had declined by 75% in lettuce, 37% in turnip roots, 54% in wheat grain, and 48% in wheat hay.

In the limited field rotational crop trials, maximum storage intervals for residue samples prior to analysis were 11-17 months for diflubenzuron, 10-13 months for CPU, and 16-22 months for PCA (Table 11).

The available storage stability data on diflubenzuron and CPU adequately support the residue data from the rotational crop field trials. However, these data do not support the PCA residue data as the residue samples were held for intervals well in excess of the intervals represented in the storage stability study. In addition, the storage stability data indicate that major declines (37-75%) can occur in PCA residues after just 12 months of storage.

Table 8. Storage Stability of diflubenzuron in fortified (0.1 ppm) control samples of rotational crops.

Commodity	Storage interval (days)	% Recovery		
		Freshly fortified samples	Stored fortified samples	Average corrected recovery [a]
Lettuce	0	91, 83	-- [b]	--
	32	76, 73	92, 113	137
	112	118, 96	61, 63	58
	206	42, 45	58,61	135
	266	85, 66	87,86	114
	380	69, 80	82, 94	117
Turnip roots	0	78, 79	--	--
	32	93, 108	82, 113	96
	112	78, 85	48, 37	52
	206	80, 76	61, 67	82
	276	89, 60	83, 75	106
	378	83, 72	82, 71	98
Wheat grain	0	96, 83	--	--
	31	114, 119	155, 159	134
	135	122, 122	49, 47	39
	206	54, 64	57, 60	99
	276	72, 74	56, 76	91
	382	77, 77	54, 82	89
Wheat hay	0	102, 102	--	--
	31	122, 122	146, 151	122
	135	98, 90	66, 58	66
	203	75, 76	52 [c]	69
	276	70, 72	70, 73	101
	394	61, 70	41, 56	73

[a] Average recovery from stored samples corrected for average concurrent method recovery.

[b] Not applicable.

[c] Only one sample recovery was reported due to inaccurate fortification.

Table 9. Storage Stability of CPU in fortified (0.1 ppm control samples of rotational crops.

Commodity	Storage interval (days)	% Recovery		
		Freshly fortified samples	Stored fortified samples	Average corrected recovery [a]
Lettuce	0	87, 89	-- [b]	--
	28	108, 107	106, 107	98
	93	107, 105	71, 75	69
	191	127, 124	91, 93	73
	271	71, 71	65, 67	93
	341	106, 97	81, 79	78
Turnip roots	0	88, 85	--	--
	28	91, 81	92, 93	108
	93	99, 99	80, 73	77
	183	96, 86	89, 89	97
	271	88, 95	90, 81	93
	341	104, 101	119, 104	109
Wheat grain	0	76, 79	--	--
	34	74, 67	39, 67	96
	89	103, 97	31, 31	31
	187	76, 72	33, 30	42
	278	82, 95	52, 48	56
	391	84, 77	39, 44	51
Wheat hay	0	89, 77	--	--
	28	89, 86	124, 123	140
	96	117, 94	93, 100	91
	187	80, 76	45, 41	55
	293	108, 123	108, 106	92
	356	80, 82	65, 73	85

[a] Average recovery from stored samples corrected for average concurrent method recovery.

[b] Not applicable.

Table 10. Storage Stability of PCA in fortified (0.1 ppm) control samples of rotational crops.

Commodity	Storage interval (days)	% Recovery	
		Freshly fortified samples	Stored fortified samples
Lettuce	0	96, 94	-- [a]
	29	97 [b]	42, 43 (43) [c]
	102	101, 98	29, 26 (27)
	182	97, 95	32, 28 (30)
	273	92, 93	33, 31 (32)
	358	95, 94	26, 25 (25)
Turnip roots	0	101, 99	--
	29	100, 98	80, 76 (78)
	91	102, 100	72, 71 (72)
	182	96, 94	70, 71 (71)
	274	89, 88	67, 65 (66)
	358	93, 102	64, 61 (63)
Wheat grain	0	99, 99	--
	30	97, 97	68, 68 (68)
	93	103, 104	46, 45 (46)
	178	97, 95	54, 47 (50)
	276	97, 99	36, 63 (50)
	351	77, 95	50, 42 (46)
Wheat hay	0	101, 102	--
	30	99, 102	68, 70 (69)
	93	100, 98	55, 54 (54)
	178	104, 102	61, 58 (59)
	276	94, 89	50, 55 (52)
	351	102, 90	51, 52 (52)

[a]Not applicable.
[b]one sample was lost due to analyst's error.
[c]Values in parentheses are the average recovery from the stored fortified samples; residues of PCA in stored samples were not corrected for recoveries from fresh fortifications as the analytical method uses an internal standard for quantifying residues.

Table 11. Range of storage intervals for samples from the rotational crop study[a].

Matrix	Storage Intervals (days) [a]		
	Diflubenzuron	CPU	PCA
Lettuce	153-343	98-301	228-578
Turnip tops	151-470	61-341	221-545
Turnip roots	203-513	54-405	253-632
Wheat forage	135-426	91-407	335-629
Wheat hay	89-426	90-400	221-597
Wheat grain	95-361	121-332	184-483
Wheat straw	77-365	83-372	307-684

[a]Although the entire range of storage intervals is given, storage intervals for the majority of samples for any given commodity were closer to the maximum interval listed than the minimum.
[b]Storage interval from harvest to analysis of a given analyte; separate extractions and analyses were conducted for each analyte.

Field Accumulation in Rotational Crops

Based upon the available data from the confined rotational crop study, the diflubenzuron RED (3/15/95) required limited rotational crop field trials in order to assess the need for tolerances for residues in rotational crops. In response, Uniroyal Chemical Company has submitted data (1998, MRID 44689703) depicting diflubenzuron residues in representative rotational crops from two limited field trials. The in-life phases of the study were conducted by ABC Laboratories (Madera, CA) and Coastal Ag Research, Inc. (Bernard, TX); the analytical phase was conducted by PTRL West, Inc. (Richmond, CA).

The rotational field trials were conducted on sandy loam soils in Madera, CA and Bernard, TX. At the CA test site, a single control plot and two treated plots were separately established for each PBI, for a total of 7 control plots and 14 treated plots. At the TX test site, one large control plot and two large treated plots were established; these large plots were each subdivided into 7 subplots, one for each PBI. Cotton was planted as the primary crop at both test sites as it has the highest labeled use rate for diflubenzuron of any rotated crop (0.375 lb ai/A/season).

Broadcast foliar applications of diflubenzuron (25% WP) were applied to the primary cotton crop beginning at the pinhead square stage in CA and at post-pinhead stage in TX. Each crop received a

total of six applications at 0.063 lb ai/A/application for a total of 0.375 lb ai/A/season (1X the maximum seasonal rate). Applications were made in 12-15 gal of water/A using ground equipment at 7- to 45-day retreatment intervals, with the final three applications being made at ~28, 21, and 14 days prior to projected crop maturity. Cotton lint was harvested from the TX plot, and the cotton plants at both sites were mowed down and disced into the soil within 25 days of the final application.

At each test site, the single control and duplicate treated subplots were planted with lettuce, turnips, and wheat as representative rotational crops at PBIs of approximately 30, 45, 60, 90, 120, 180, and 365 days after the final application of diflubenzuron. The crops received water, fertilizer, and maintenance pesticides as necessary; adequate information pertaining to the growing conditions was provided.

With some exceptions, a single control and four treated samples (two treated samples/plot) of the various RACs for each crop were harvested from each PBI at each test site. Lettuce samples were harvested at maturity 81-153 days after planting (DAP). Turnips were also harvested at maturity (81-153 DAP) and separated into roots and tops. Wheat forage was sampled at 49-62 DAP. Wheat hay was harvested at the early milk or dough stage (78-237 DAP) and was air dried for 4 to 7 days prior to sampling. Wheat grain and straw samples were collected at maturity (128-269 DAP).

The petitioner reported that samples of wheat forage were inadvertently not collected from the 30-, 45-, and 60-day PBIs at the TX site, and that adverse weather conditions or animal damage resulted in the loss or reduced the yield of the following samples from the TX site: 120-day PBI lettuce; 120- and 180-day turnip roots and tops; 90- and 120-day wheat forage; 90-, 120-, and 180-day PBI wheat hay; 90-, 120-, and 180-day grain and straw; and 365-day grain. A hard frost also resulted in the loss of the 365-day PBI wheat grain samples from CA.

Crop samples were placed on blue ice in coolers and frozen within 5 hours of collection. Prior to shipment, crop samples were stored at <0 °C at the field test sites for 1-50 days with the following exceptions: 60-day PBI turnips from CA (280 days), 365-day PBI wheat hay from CA (98 days), and 365-day wheat forage from TX (138 days). Samples were shipped by freezer truck from the field sites to the analytical laboratory. Samples from the 30-day through 180-day PBIs were initially shipped to Colorado Analytical Research and Development Corp. (Colorado Springs, CO), which was originally planned to be the analytical laboratory. When PTRL West was selected as the analytical laboratory, these samples were transferred by freezer truck to PTRL. The remaining samples at the field sites were shipped by freezer truck directly to PTRL. All samples were stored at <0 °C at PTRL until samples analysis. As

indicated above (Table 11), the maximum frozen storage intervals for the crop samples ranged from 11-17 months for analysis of diflubenzuron, 10-13 months for analysis of CPU, and 16-22 months for analysis of PCA.

Residues of diflubenzuron, CPU, and PCA were determined in the treated and control samples using the adequate GC/ECD or GC/MS methods discussed above. An analytical sample set consisted of the single control sample, two fortified control samples, and the four treated samples from a given PBI at each test site. Residues of diflubenzuron and CPU in rotational crops are presented in Table 12. Residues of PCA were <LOQ (<5 ppb) in all rotational crop commodities.

In lettuce, residues of diflubenzuron were <0.01 ppm except in two out of four samples from the 45-day PBI in CA, which had residues of 0.01 and 0.02 ppm. Residues of CPU were also <0.01 ppm in all samples except for two samples from the 90-day PBI in CA, which had residues of 0.01 and 0.02 ppm. Apparent residues of both diflubenzuron and CPU were <LOQ in all control samples of lettuce.

Residues of diflubenzuron were <0.01 ppm in turnip roots and tops, except in one sample of tops from CA (180-day PBI). Apparent residues of diflubenzuron were also <LOQ in all control samples. In turnip tops, residues of CPU were detected at 0.01-0.03 ppm in all treated samples from the 30- through the 180-day PBIs in CA and from the 60- and 90-day PBIs in TX. However, the control samples associated with these samples also had apparent residues of CPU at the same levels (0.01-0.03 ppm). A similar situation was noted in turnip roots. Residues of CPU were detected at 0.01-0.04 ppm in treated samples from the 30- through 120-day PBIs in CA and at 0.01-0.06 ppm in samples from the 30- and 60-day PBIs in TX. Seven out of the 12 turnip root controls had apparent residues of CPU at 0.01-0.03 ppm. Although the method recovery data for CPU in turnips indicates that an LOQ of 0.01 ppm is acceptable for roots and tops, the apparent residues of CPU in these control samples suggests that the LOQ for CPU should be at least 0.03 ppm.

In wheat forage, residues of diflubenzuron were detected at 0.01 ppm in three samples from the 90-day PBI in CA, in two samples from the 120-day PBI in CA, and in one sample each from the 365-day PBI in CA and the 180-day PBI in TX. However, apparent residues of diflubenzuron at 0.01 ppm were also detected in the three control samples from CA that were associated with these treated samples. With one exception, diflubenzuron residues in the remaining 29 forage samples were <0.01 ppm. One treated sample from the 30-day PBI in CA also had diflubenzuron residues at 0.10 ppm; however, there was a discrepancy between this value in the report summary tables and the analytical laboratory's data sheets. Residues of CPU were detected at 0.01-0.02 ppm in 10 forage samples from the 30- through 90-day PBIs from CA. Residues of CPU were not detected

in forage samples from TX; however, forage samples from the 30- through 120-day PBIs were unavailable from the TX test site. Apparent residues of CPU were <LOQ in all control samples of forage.

In wheat hay, residues of diflubenzuron and CPU were <0.01 ppm in all treated samples, and apparent residues of diflubenzuron were <LOQ in all control samples except for one control sample from TX with apparent residues of diflubenzuron at 0.01 ppm.

In wheat grain, diflubenzuron was detected at 0.01 ppm in one sample from CA at the 180-day PBI and in the four samples from the 45-day PBI in TX; however, the 45-day PBI control sample from TX also had apparent residues of diflubenzuron at 0.01 ppm. Diflubenzuron was <0.01 ppm in the remaining 32 treated grain samples. One sample from the 30-day PBI in CA had residues of CPU at 0.02 ppm; CPU residues were <0.01 ppm in the remaining 35 grain samples. Apparent residues of CPU were <LOQ in all control samples of grain.

Diflubenzuron was detected at 0.01 ppm in 10 wheat straw samples from various PBI in CA and from the 30-day PBI in TX; however, with one exception, the six control samples associated with these treated samples also had apparent residues of diflubenzuron at 0.01 ppm. Diflubenzuron was <0.01 ppm in the remaining 32 treated straw samples. One straw sample from the 45-day PBI in TX had residues of CPU at 0.02 ppm; CPU residues were <0.01 ppm in the remaining 41 straw samples. Apparent residues of CPU were <LOQ in all control samples of straw.

Table 12. Diflubenzuron residues in representative rotational crops planted following repeated foliar applications of diflubenzuron (25% WP) to cotton totaling 0.375 lb ai/A/season (1X maximum seasonal rate) [a].

Crop/ commodity	PBI (days)	Diflubenzuron (ppm)		CPU (ppm)	
		CA	TX	CA	TX
Lettuce	30	<0.01, <0.01,<0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	45	<0.01, <0.01, **0.01, 0.02** [b]	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	90	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, **0.02, 0.01**, <0.01	<0.01, <0.01, <0.01, <0.01
	120	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	180	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	365	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
Turnip tops	30	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.02, 0.02, 0.01, 0.01** (0.024) [d]	<0.01, <0.01, <0.01, <0.01
	45	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.01, 0.01, 0.01, 0.01** (0.013)	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.02, 0.02, 0.02, 0.02** (0.012)	**0.03, 0.03, 0.03, 0.03** (0.024)
	90	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.01, 0.01, 0.01, 0.01** (0.013)	**0.02, 0.02, 0.01, 0.01** (0.025)
	120	<0.01, <0.01, <0.01, <0.01	No samples [c]	**0.03, 0.03, 0.03, 0.03** (0.033)	No samples [c]
	180	<0.01, <0.01, <0.01, **0.01**	No samples [c]	**0.03, 0.03, 0.02, 0.02** (0.024)	No samples [c]
	365	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
Turnip roots	30	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.04, 0.01**, <0.01, <0.01 (0.034)	**0.06, 0.01, 0.02, 0.01** (0.010)
	45	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.01, 0.02, 0.01, 0.01** (0.012)	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.02, 0.02, 0.02, 0.02** (0.018)	<0.01, <0.01, <0.01, **0.01** (0.016)
	90	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	**0.02, 0.02**, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	120	<0.01, <0.01, <0.01, <0.01	No samples [c]	**0.01, 0.01, 0.01, 0.02** (0.012)	No samples [c]
	180	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01 (0.026)	No samples [c]
	365	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
Wheat forage	30	<0.01, <0.01, <0.01, **0.10** [e]	No samples [f]	**0.01, 0.01, 0.01, 0.01**	No samples [f]
	45	<0.01, <0.01, <0.01, <0.01	No samples [f]	<0.01, **0.02, 0.01, 0.01**	No samples [f]
	60	<0.01, <0.01, <0.01, <0.01	No samples [f]	**0.01**, <0.01, <0.01, <0.01	No samples [f]
	90	**0.01, 0.01, 0.01**, <0.01 (0.011)	No samples [c]	**0.01, 0.02**, <0.01, <0.01	No samples [c]
	120	**0.01, 0.01**, <0.01, <0.01 (0.012)	No samples [c]	<0.01, <0.01, <0.01, <0.01	No Samples [c]
	180	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, **0.01**, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	365	<0.01, <0.01, **0.01**, <0.01 (0.011)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01

(Continued; footnotes follow)

Crop/ commodity	PBI (days)	Diflubenzuron (ppm)		CPU (ppm)	
		CA	TX	CA	TX
Wheat hay	30	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	45	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	90	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	120	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	180	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	365	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01 (0.011)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
Wheat grain	30	<0.01, <0.01, <0.01, <0.01 (0.012)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, **0.02**, <0.01	<0.01, <0.01, <0.01, <0.01
	45	<0.01, <0.01, <0.01, <0.01	**0.01, 0.01, 0.01, 0.01** (0.011)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	90	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	120	<0.01, <0.01, <0.01, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	180	<0.01, <0.01, **0.01**, <0.01	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	365	No samples [c]	<0.01 (0.010)	No samples [c]	No samples [c]
Wheat straw	30	<0.01, <0.01, <0.01, <0.01 (0.011)	**0.01, 0.01, 0.01, 0.01** (0.012)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	45	<0.01, <0.01, <0.01, **0.01** (0.015)	<0.01, <0.01, <0.01, <0.01	<0.01, **0.02**, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	60	<0.01, <0.01, <0.01, <0.01 (0.011)	<0.01, <0.01, <0.01, <0.01 (0.011)	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01
	90	<0.01, **0.01, 0.01, 0.01** (0.010)	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	120	<0.01, <0.01, <0.01, **0.01** (0.012)	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	180	<0.01, <0.01, <0.01, **0.01**	No samples [c]	<0.01, <0.01, <0.01, <0.01	No samples [c]
	365	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01	<0.01, <0.01, <0.01, <0.01	<0.01, <0.01

[a] All crop samples were also analyzed for residues of PCA, which were <LOQ (<5 ppb) in all samples.

[b] **Bolded** values are samples with residues ≥LOQ.

[c] No samples were obtained due to crop failure.

[d] Values listed in parentheses are apparent residues of diflubenzuron or CPU detected in control samples that are ≥LOQ.

[e] Value was reported as 0.01 ppm report in summary table, but was given as 0.098 ppm in data spread sheet (MRID 44689703, p. 1011) from analytical laboratory.

[f] No samples of wheat forage were collected from the 30-120 day PBI at the TX test site.

HED's Conclusion: HED noted the following deficiencies in the limited rotational field trials: (i) samples were held frozen for up to 16-22 months prior to analysis of PCA and the available storage stability data indicate that PCA is not stable in any commodity after one month of frozen storage; (ii) lack of forage samples for wheat from the TX field site from the 30-day to 120-day PBIs; and (iii) for one of the 30-day forage samples from CA, there is an apparent discrepancy in the residue value for diflubenzuron between the residue summary table and the analytical laboratory's data sheets.

Although the PCA data in the above study are questionable, HED will not reject the study on this basis as the available metabolism data indicate that PCA is a minor component of the residue compared to diflubenzuron and CPU. PCA was not detected in the primary plant metabolism studies on citrus and soybeans. In addition, PCA (conjugated) was only a minor component of the total radioactive residue (TRR) in rice grain (0.3% TRR) and straw (1.5% TRR); whereas, free diflubenzuron and CPU, respectively, accounted for 0.3 and 22% of the TRR in rice grain and 41.9 and 28.6% of the TRR in rice straw. PCA was also not detected in any crops in the confined rotational crop study.

Although residues of diflubenzuron or CPU were found above the LOQ (0.01 ppm) in a number of samples of lettuce, turnip roots and tops, and wheat grain and straw, the residue levels in these samples were generally low ($\leq$0.06 ppm) and the associated control samples usually bore apparent residues at similar levels. Out of the 307 samples analyzed for residues of diflubenzuron, a total of 26 samples had residues at 0.01-0.02 ppm, with the exception of one questionable residue value for a forage sample (0.1 ppm). Of these 26 samples, 19 were associated with control samples bearing apparent residues at 0.01-0.02 ppm, and the remaining 7 samples bore residues at 0.01-0.02 ppm. Out of the 306 samples analyzed for residues of CPU, a total of 67 samples had residues of CPU at 0.01-0.06 ppm. Of these 67 samples, 51 were associated with control samples bearing apparent residues at 0.01-0.03 ppm, and the remaining 16 samples bore CPU residues at 0.01-0.02 ppm.

Given the low number of samples bearing residues of diflubenzuron or CPU and the low levels (0.01-0.06 ppm) of these residues, HED concludes that quantifiable residues of diflubenzuron, CPU and PCA are unlikely to occur in rotated crops planted at least 30 days following the final application of diflubenzuron to the primary crop.

Provided the petitioner explains the discrepancy in the 0.10 ppm residue value reported for diflubenzuron in one of the wheat forage samples from CA, the limited field rotational crop study is adequate. The available data indicate that tolerances for diflubenzuron residues in rotational crops will not be required

provided the Dimilin labels specify a restriction for the planting of rotation crops of at least 30 days. The current label specifies a rotational crop restriction which prohibits the planting of food or feed crops for 6 months following the last application unless it is labeled for use on that crop. This deficiency is now resolved.

cc: PP#8F04925, G. Kramer (RAB1), J. Rowell (RAB1), diflubenzuron List A File
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Chemical:	**Diflubenzuron**
PC Code:	**108201**
HED File Code	**11100 Other Chemistry Documents**
Memo Date:	**02/17/99**
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